Chain Transfer Constants for Vinyl Monomers Polymerized in Methyl Oleate and Methyl Stearate

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Synopsis

Chain transfer constants were obtained for styrene, methyl methacrylate, methyl acrylate and vinyl acetate, polymerized in methyl oleate and methyl stearate at 60°C. Transfer constants increased in the order: methyl methacrylate < styrene < methyl acrylate ≪ vinyl acetate in both solvents. Average values of the transfer parameters were: for methyl oleate, $Q_{tr} = 2.04 \times 10^{-4}$, $e_{tr} = 1.08$; for methyl stearate, $Q_{tr} = 0.373 \times 10^{-4}$, $e_{tr} = 1.01$. Indication that polar species predominate in the transition state is supported by the observed order of reactivity The usual rate dependence appeared to be followed by all of the monomers except vinyl acetate, which was retarded, severely in methyl oleate. Transfer in methyl oleate was about 5.8 times greater than that found in methyl stearate for these four monomers. The internal allylic double bond of methyl oleate had about the same reactivity in transfer as had the terminal unsaturation in N-allylstearamide at 90°C. Rough estimates were obtained of the monomer transfer constants for the long side-chain homologs of these four monomers from the respective monomer transfer constants and the experimental transfer constants, corrected for transfer to the labile groups of the solvent. It was concluded that the rate of polymerization would determine in large measure the degree of polymerization for the reactive 18-carbon homologs but that the molecular weight of poly(vinyl stearate) and (oleate) will be regulated primarily by transfer to monomer.

INTRODUCTION

Few determinations are available of chain transfer constants for vinyl monomers polymerized in saturated and unsaturated esters.[1a] Studies with saturated esters include those of styrene polymerized in ethyl acetate,[2] methyl methacrylate in ethyl acetate,[3,4] and vinyl acetate in ethyl acetate,[5-8] a variety of esters including methyl n-butyrate,[8] n-amyl acetate,[9] and selected n-alkyl acetate homologs.[10] Values of the transfer constant were generally small (ca. 0.4 to 3 $\times$ 10^{-4}), increasing with decreasing monomer reactivity[2-7] and increasing length of the acyl group.[8,9] However, in one work,[10] where the length of the n-alkyl group in a series of n-alkyl acetates was varied, the labile α-methylene group alone appeared to determine the magnitude of the transfer constant. Only two papers[11,12] compared transfer constants for two structurally different radicals toward a common solvent (ethyl acetate). Of special significance to this work was

the observation[13] that transfer constants for vinyl acetate increased proportionately as the side-chain length increased, when ethyl esters of the homologous series of fatty acids were used as solvents.

Even fewer studies were made of chain transfer in unsaturated systems. The available data included vinyl acetate polymerized in allyl acetate, in methyl oleate, and in selected alkenes;[8] styrene[14] and methyl methacrylate[15] in several alkenes, and four vinyl monomers in N-allylstearamide.[16]

In this work are reported chain transfer constants and transfer parameters for styrene, methyl methacrylate, methyl acrylate, and vinyl acetate polymerized at 60°C in methyl oleate and in methyl stearate. This choice of monomers should define the relative magnitude of transfer of radicals having a wide range of reactivity toward a saturated and unsaturated ester of otherwise identical structure. The corresponding degree of rate retardation should reflect on the ease of addition of the two solvent radicals to these monomers. Comparison can also be made of transfer by the methylene-flanked, internal double bond of methyl oleate, and the external allylic double bond of N-allylstearamide.[16] The recent observation[17] that homopolymers and copolymers having 18-carbon oleyl side chains do not exhibit side-chain crystallinity gave added impetus to this investigation. Side-chain crystallinity characterizes the linear alkyl side-chains of equal carbon length. This often leads to undesirable embrittlement in copolymers made by use of fat-derived vinyl monomers.[18] Therefore, it seemed important to know the extent of transfer and rate retardation to be expected for various radicals in the presence of unsaturation in the side chain. Finally, if transfer by the long side chains can be isolated, rough approximations of the monomer transfer constants can be calculated for 18-carbon homologs of these four monomers.

EXPERIMENTAL

Materials

Methyl oleate was purchased from Applied Science Laboratories and was 99.7% pure by gas–liquid chromatography, mp −19.9°C, and contained no *trans-* isomer by infrared analysis.

Methyl stearate was obtained by esterification of stearic acid (Hystyrene, Humpko Products), twice crystallized from acetone (10 ml/g) at 0°C. The stearic acid was esterified with a 7 mole ratio of methyl alcohol, with the use of 2% sulfuric acid as catalyst and 4 hr reflux time, isolated in excess hot water; the crude product was twice crystallized (10 ml/g) from acetone at 0°C to yield the ester in 74% yield, 99% pure by gas–liquid chromatography. The saponification number was 186.8 and the melting point was 39–40°C.

Polymerization Procedure

The procedure previously described[16] was used, and similar sample weights of monomer and solvent were employed, although in some cases the

quantities were doubled. Most of the polymerizations were conducted at 60°C. No thermal polymerization was noted at this temperature. Some poly(methyl methacrylate) precipitated in both solvents; a little gel was found for methyl acrylate polymerized in methyl stearate. All of the other polymers were soluble. The polymers were isolated and freed of the fatty ester by extraction with hot methanol (5 ml/g), except for methyl acrylate, which was treated with hot Skellysolve B. Usually five or six extractions with hot petroleum ether were carried out to remove solvent from the vinyl acetate polymers; products obtained in methyl oleate were extracted five or six times with n-hexane at room temperature. These experiments were repeated with the use of a single room-temperature extraction as in the technique employed by Clarke.[8] Because similar molecular weights were obtained in both sets, it was concluded that low molecular weight polymer was not being extracted and lost through the repeated extractions. Elemental analyses were obtained on selected polymers and yielded the expected values.

Solution Properties

The procedure of Jordan et al.[16] was followed by use of a Mechrolab osmometer. Intrinsic viscosities in benzene at 25°C were obtained from ArRo Laboratories on the methyl methacrylate polymers polymerized in methyl stearate at 60°C.

Computations

The regression parameters and their intercepts for eqs. (1), (3), and (4) were evaluated by an IBM 1130 computer using program designation VGM-58 and were carried through third-degree polynomials. Programs for the remaining calculations were written for insertion in a general calculation subroutine designated QREAD.

RESULTS AND DISCUSSION

Experimental Results and Rate Data

All transfer and rate data are given in Table I for the monomers polymerized in methyl oleate and in Table II for the polymerizations carried out in methyl stearate. Values of the chain transfer constants for these monomers in both solvents are listed in Table III. Transfer constants were obtained by using the equation of Mayo,[19]

$$1/\bar{X}_n = 1/\bar{X}_{n0} + C_S[S]/[M] \tag{1}$$

where $1/\bar{X}_n$ is the reciprocal number-average molecular weight, $[S]/[M]$ is the solvent–monomer ratio, and C_S is the chain transfer constant. $1/\bar{X}_{n0}$ is defined as

$$1/\bar{X}_{n0} = C_M + k_t/k_p^2 R_p/[M]^2 \tag{2}$$

TABLE I
Transfer and Rate Data for Selected Vinyl Monomers Polymerized in Methyl Oleate at 60°C

Experiment	Transfer data				Rate data			
	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	$[S]/[M]$	Conversion, %	$[M]$, mole/kg	$[I] \times 10^3$, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
				Styrene, no added initiator, 90°C				
1	484 900	0.215	0	9.09	9.60	0	0.303	0.329
2	248 400	0.419	0.240	10.9	5.71		0.429	1.32
3	175 700	0.593	0.495	10.4	3.99		0.287	1.80
4	113 300	0.919	0.975	9.88	2.54		0.145	2.23
5	71 200	1.46	1.86	8.78	1.53		0.068	2.90
6	43 300	2.41	3.92	7.37	0.79		0.021	3.35
			Styrene, [benzoyl peroxide]/[monomer] = 3.54 × 10⁻⁴					
7	331 200	0.314	0	6.55	9.60	3.62	0.250	0.271
8	228 900	0.455	0.254	7.42	5.57	2.03	0.128	0.411
9	223 700	0.466	0.507	8.77	3.93	1.48	0.080	0.516
10	152 300	0.684	1.00	9.88	2.50	0.911	0.038	0.611
11	107 500	0.969	1.93	9.03	1.48	0.522	0.016	0.707
12	65 150	1.60	4.03	8.54	0.77	0.283	0.004	0.642
			Styrene, [AIBN]/[monomer] = 3.63 × 10⁻⁴					
13	234 900	0.443	0	9.74	9.60	3.58	0.433	0.470
14	208 300	0.500	0.247	9.63	5.64	2.05	0.201	0.632
15	185 400	0.562	0.491	8.95	4.01	1.45	0.111	0.690
16	134 400	0.775	1.01	10.4	2.48	0.905	0.051	0.833
17	89 500	1.16	1.95	10.9	1.47	0.529	0.019	0.902
18	59 100	1.76	3.86	11.8	0.80	0.283	0.005	0.848

No.								
Methyl methacrylate, [AIBN]/[monomer] = 3.38×10^{-4}								
19	813 900	0.123	0	10.9	9.99	3.55	1.65	1.66
20	462 700	0.216	0.247	11.8	5.77	2.05	0.874	2.63
21	556 000	0.180	0.489	12.1	4.08	1.45	0.782	4.69
22	513 700	0.195	0.954	10.9	2.61	0.897	0.394	5.78
23	261 300	0.383	1.84	8.36	1.55	0.535	0.120	4.99
24	126 500	0.791	3.89	8.54	0.80	0.280	0.027	4.24
Methyl acrylate, [AIBN]/[monomer] = 3.66×10^{-4}								
25	264 700	0.325	0	5.15	11.62	4.26	0.511	0.379
26	122 300	0.704	0.252	5.30	6.22	2.28	0.183	0.473
27	135 600	0.635	0.502	5.58	4.26	1.56	0.097	0.533
28	94 550	0.911	1.01	7.11	2.60	0.954	0.057	0.844
29	92 350	0.932	1.99	5.26	1.48	0.541	0.012	0.548
30	44 000	1.96	3.90	5.04	0.80	0.296	0.003	0.405
Vinyl acetate, [AIBN]/[monomer] = 3.61×10^{-4}								
31	340 400	0.253	0	9.27	11.62	4.21	9.06	6.72
32	376 500	0.229	0	8.38	11.62	4.21	9.01	6.68
33	99 000	0.870	0.0209	10.2	10.84	3.89	0.577	0.492
34	98 850	0.871	0.0211	7.80	10.83	3.92	0.521	0.445
35	66 300	1.30	0.0426	10.3	10.13	3.68	0.276	0.269
36	71 100	1.21	0.0424	8.40	10.14	3.67	0.249	0.242
37	46 950	1.83	0.0657	9.22	9.47	3.42	0.157	0.174
38	45 400	1.90	0.0638	8.63	9.52	3.42	0.146	0.161
39	43 000	2.00	0.0866	11.2	8.95	3.24	0.107	0.134
40	37 600	2.29	0.0871	9.49	8.94	3.21	0.096	0.120
41	33 275	2.59	0.116	9.53	8.30	2.99	0.065	0.094
42	28 850	2.98	0.111	9.34	8.40	3.04	0.066	0.094

TABLE I (continued)

Experiment	Transfer data				Rate data			
	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	$[S]/[M]$	Conversion, %	$[M]$, mole/kg	$[I] \times 10^3$, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
			Vinyl acetate, $[AIBN]/[monomer] = 3.61 \times 10^{-4}$, 90°C					
43	181 730	0.478	0	9.40	11.62	4.16	178.4	132.2
44	70 550	1.22	0.0208	7.94	10.84	3.93	31.9	27.1
45	46 750	1.84	0.0425	7.55	10.13	3.63	11.8	11.5
46	37 000	2.33	0.0642	9.77	9.51	3.45	6.15	6.79
47	31 750	2.71	0.0876	7.91	8.92	3.24	2.93	3.68
48	27 550	3.13	0.1125	8.21	8.37	3.02	1.14	1.63

TABLE II
Transfer and Rate Data for Selected Vinyl Monomers Polymerized in Methyl Stearate at 60°C

Experiment	Transfer data				Rate data			
	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	$[S]/[M]$	Conversion, %	$[M]$, mole/kg	$[I] \times 10^3$, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
Styrene, no added initiator, 90°C								
1	459 200	0.227	0	9.31	9.60	0	0.292	0.317
2	932 550	0.112	0.252	7.95	5.58		0.107	0.344
3	777 450	0.134	0.508	7.95	3.91		0.054	0.353
4	477 200	0.218	0.984	8.09	2.51		0.022	0.344
5	462 800	0.225	1.90	8.28	1.49		0.009	0.387
6	282 050	0.369	3.84	28.4	0.80		0.002	0.290
Styrene, $[\text{AIBN}]/[\text{monomer}] = 3.62 \times 10^{-4}$								
7	194 200	0.536	0	9.89	9.60	3.48	0.480	0.520
8	253 700	0.410	0.248	8.24	5.61	2.02	0.183	0.583
9	245 400	0.424	0.503	10.3	3.93	1.43	0.118	0.764
10	195 500	0.533	1.000	9.46	2.49	0.908	0.047	0.754
11	153 400	0.679	1.96	10.02	1.45	0.523	0.017	0.815
12	131 400	0.790	3.97	11.24	0.78	0.280	0.005	0.856
Methyl methacrylate, $[\text{AIBN}]/[\text{monomer}] = 3.52 \times 10^{-4}$								
13	1 290 000	0.0776	0	11.3	9.99	3.63	1.79	1.79
14	4 689 000	0.0213	0.245	12.5	5.77	2.03	1.71	5.14
15	3 030 000	0.0330	0.495	12.2	4.03	1.44	1.64	10.1
16	1 683 000	0.0595	0.970	12.9	2.57	0.91	0.69	10.5
17	1 237 000	0.0809	1.88	10.2	1.51	0.52	0.26	11.3
18	818 900	0.1222	3.71	12.7	0.83	0.28	0.10	15.0

(continued)

TABLE II (continued)

Experiment	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	[S]/[M]	Conversion, %	[M], mole/kg	[I] $\times 10^3$, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
		Transfer data				Rate data		
			Methyl acrylate, [AIBN]/[monomer] = 3.57 $\times 10^{-4}$					
19	336 700	0.256	0	7.81	11.62	4.18	0.746	0.553
20	287 700	0.299	0.248	10.6	6.25	2.26	0.293	0.750
21	396 100	0.217	0.493	11.6	4.29	1.55	0.197	1.08
22	356 500	0.241	0.981	9.50	2.64	0.955	0.119	1.71
23	271 800	0.317	1.92	12.4	1.52	0.538	0.070	3.01
24	160 300	0.537	3.72	12.4	0.83	0.288	0.015	2.15
			Vinyl acetate, [AIBN]/[monomer] = 3.59 $\times 10^{-4}$					
25	303 000	0.284	0	8.13	11.62	4.21	8.20	6.08
26	227 000	0.379	0.0224	8.61	10.79	3.89	6.00	5.16
27	179 900	0.479	0.0429	10.5	10.11	3.68	5.08	4.97
28	159 900	0.539	0.0656	10.0	9.47	3.38	3.93	4.39
29	134 100	0.642	0.0888	11.3	8.88	3.18	3.03	3.84
30	120 300	0.716	0.113	10.9	8.35	3.00	2.52	3.62
31	84 500	1.02	0.251	9.45	6.21	2.24	0.98	2.53
32	64 050	1.34	0.492	13.9	4.29	1.53	0.47	2.56
33	41 250	2.09	0.967	11.2	2.67	0.946	0.13	1.79
34	25 980	3.32	1.97	12.4	1.49	0.538	0.03	1.22

TABLE III
Transfer and Kinetic Constants for Selected Vinyl Monomers Polymerized in Methyl Oleate and Methyl Stearate at 60°C

Monomer	Solvent	Transfer constants[a]		Kinetic constants[b]	
		$C_S \times 10^4$	$1/\bar{X}_{n0} \times 10^4$	a	$\ln K$
Styrene, thermal, 90°C	Me Oleate	6.64 ± 0.19	2.48 ± 0.19	1.10 ± 0.06	−9.79 ± 0.17
Styrene, benzoyl peroxide	"	3.15 ± 0.09	3.42 ± 0.19	1.17 ± 0.04	−9.27 ± 0.10
Styrene, AIBN	"	3.52 ± 0.11	4.25 ± 0.20	1.08 ± 0.12	−7.79 ± 0.32
Methyl methacrylate	"	1.68 ± 0.17	1.07 ± 0.31	1.30 ± 0.10	−9.29 ± 0.25
Methyl acrylate	"	3.66 ± 0.52	4.44 ± 0.96	5.37 ± 0.27	−7.84 ± 0.16
Vinyl acetate	"	217.0 ± 11.8	3.38 ± 0.79	9.76 ± 0.80	−1.64 ± 0.44
Vinyl acetate, 90°C	"	358.0 ± 16.9	4.99 ± 0.40		
Styrene, thermal, 90°C	Me Stearate	0.676 ± 0.09	1.10 ± 0.19	1.20 ± 0.03	−9.20 ± 0.08
Styrene, AIBN	"	1.06 ± 0.17	4.03 ± 0.34	0.82 ± 0.14	−7.70 ± 0.36
Methyl methacrylate	"	0.282 ± 0.03	0.222 ± 0.06	0.91 ± 0.08	−9.20 ± 0.22
Methyl acrylate	"	0.751 ± 0.18	2.19 ± 0.32	1.82 ± 0.07	−6.75 ± 0.08
Vinyl acetate	"	38.2 ± 1.44	2.95 ± 0.10		

[a] In the calculation of C_S and $1/\bar{X}_{n0}$, experiment 6 of Table I and experiments 1, 7, 13, and 31–34 of Table II were not used.
[b] In the calculation of a and $\ln K$, experiments 31 and 32 of Table I and experiments 31 and 34 of Table II were not used.

where C_M is the constant for transfer to monomer and the second term expresses the variation of $\bar{X}_n$ by the rate.

Equation (1) applies only at low conversion when a constant ratio of initiator to monomer is employed, so that $R_p/[M]^2$ [eq. (2)] stays constant. Other requirements are that low concentrations of initiator, preferably azobisisobutyronitrile, be used, and that rate retardation be minimal.[20]

Because rates of polymerization were obtained at constant ratios of initiator and monomer, exponents of the monomer and initiator concentrations in the rate expression for steady-state polymerization could not be ascertained in the usual way from the data. However, the rate law can be expressed as

$$R_p = K([M][I]^{1/2})^a \tag{3}$$

where R_p is the rate of polymerization (in mole/kg sec), $K = k_p f k_d^{1/2}/k_t^{1/2}$, and $[I]$ is the initiator concentration. No rate retardation is present when a is unity; an increase in a reflects the degree of retardation. Values of a and K, obtained as the regression coefficient and intercept, respectively, from plots of $\ln R_p$ versus $\ln [M] + 0.5 \ln [I]$, are given in Table III. Essentially no deviation from unity was found for a in all of the systems studied except those employing vinyl acetate. Here, retardation was contributed by both solvents, but methyl oleate was more rate-reducing, especially at 90°C. R_p was also found[20] to be directly proportional to $[M]^{3/2}$ for all of the monomers in both solvents, except vinyl acetate. Retardation for this unreactive monomer is not unusual.[8] Solvent radicals are often more stable than the monomer radical and addition to monomer is thereby thwarted. The kinetic treatment for this situation has been given for retardation in vinyl acetate by Allen et al.,[21] and a complete general treatment was presented by Kice.[22] Values of the retardation ratio q,[8] which is the ratio of the retardation rate to the rate in the absence of solvent at the concentration of pure monomer,

$$q = R_p/R_{p0}$$

were obtained for the vinyl acetate experiments. Values of q were 0.8–0.07 for methyl stearate and 0.07–0.01 for methyl oleate, and decreased with dilution in both solvents. Because insufficient rate data were available, the treatment of Kice[22] could not be applied. Consequently, transfer constants for vinyl acetate (Table III) may be considered only apparent[8] values.

The molecular weights for styrene and methyl methacrylate (Table II) were considerably higher at low ester concentrations than were the values for the pure monomer. Molecular weights, calculated from intrinsic viscosities run in benzene at 25°C by using a molecular weight relation,[23] confirmed these results. This appeared to be an example of diffusion-controlled termination,[24–26] introduced by the solvent viscosity, and known to be characteristic of methyl methacrylate[24] and styrene.[27] However, especially because methyl methacrylate was somewhat insoluble in both

solvents, delayed termination in precipitation polymerization[28] may be operating in this case. Even theta-solvent retardation[29] could not be dismissed as possibly contributing to the effect in styrene. While the regression coefficients for transfer for the two monomers in methyl stearate were obtained in Table III, by omitting the value for pure homopolymer (at $[S]/[M] = 0$), values of the constant could have been affected somewhat by the imposition of one of the above effects, even though the one that pertains is unknown. Of course, this reduction could be present in most of the data but be masked by the greater magnitude of transfer in the others.

Transfer Constants and Transfer Parameters

Plots of $1/\bar{X}_n$ against $[S]/[M]$, as in eq. (1), are given in Figures 1 and 2 for all of the monomers at 60°C, in both solvents. Values of the regression coefficients C_S and intercepts $1/\bar{X}_{n0}$ are given in Table III. Transfer in methyl stearate was much less than in methyl oleate, as would be expected. Relative rates were: methyl methacrylate < styrene < methyl acrylate ≪ vinyl acetate in both solvents. Except for vinyl acetate, literature values[2-8] for the short-chain homologs are similar to those found here. Consequently, the contribution of the side-chain methylene groups to the numerical value of the transfer constants is small for all of the monomers except vinyl acetate. The magnitude of the constant, found by Buselli[13] for vinyl acetate in ethyl stearate at 50°C, is higher than that found here for methyl stearate by a factor of about 3.7. The reason for this is unknown, but the intercept in the former work also seems to be unusually large. A smaller value was found in this work for vinyl acetate in methyl oleate than was previously found,[8] where C_S was reported to be 0.1.

Transfer constants for styrene, thermally polymerized at 90°C in N-allylstearamide[16] and, in the present work, in methyl oleate at the same
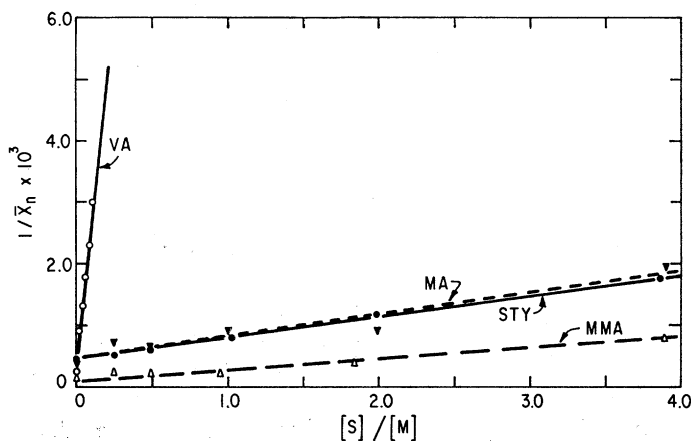

Fig. 1. Reciprocal number-average degree of polymerization vs. the solvent/monomer ratio for the monomers polymerized in methyl oleate at 60°C.
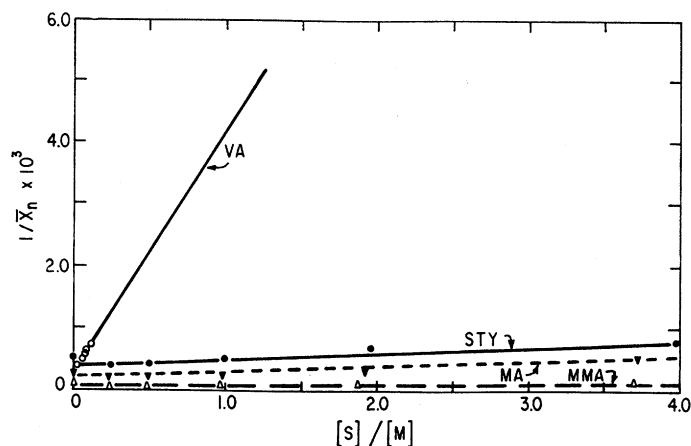
Fig. 2. Reciprocal number-average degree of polymerization vs. the solvent/monomer ratio for the monomers polymerized in methyl stearate at 60°C.
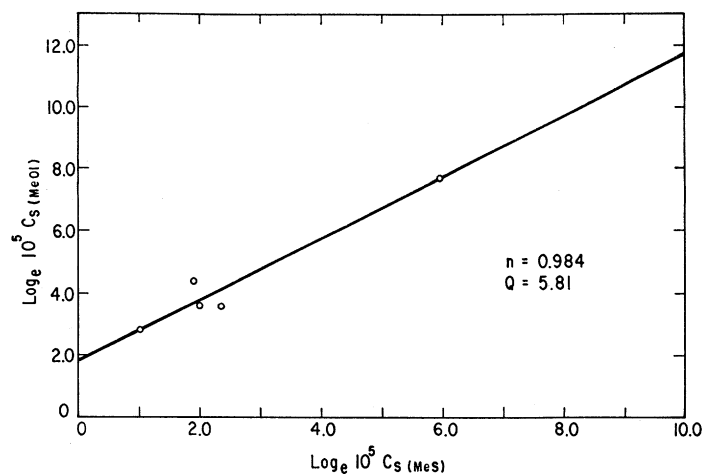

Fig. 3. Relation between the transfer constants in methyl oleate and in methyl stearate.

temperature, had similar values, being, respectively, 5.82×10^{-4} and 6.64×10^{-4}. Corresponding values for inititated vinyl acetate were somewhat different (620×10^{-4} and 358×10^{-4}, respectively). Kinetic complications of the former system[16] and structural differences might explain this lack of correspondence. Because reasonably close values were found[14] for styrene polymerized in 1- and 2-alkenes, it may be tentatively postulated that similar reactivities apply to both internal and external allylic unsaturation.

A plot of ln C_S for methyl oleate (MeOl) versus ln C_S for methyl stearate (MeS) was linear (Fig. 3) and corresponded to the relation

$$C_{S(MeOl)} = Q[C_{S(MeS)}]^n \tag{4}$$

TABLE IV
Transfer Parameters for Selected Vinyl Monomers Polymerized in Methyl Oleate and Methyl Stearate at 60°C

Monomer pairs[a]	Solvent	Transfer parameters		Specific transfer constant		Transfer constants	
		$Q_{tr} \times 10^4$	e_{tr}	Monomer	k_{tr}, kg/mole-sec	Calcd	Found
Sty–MMA	Me oleate	1.28	0.47	Sty	0.0620	9.16	3.52
Sty–MA		1.36	0.39	MMA	0.0617	2.11	1.68
Sty–VA		8.05	−1.83	MA	0.765	3.65	3.66
MMA–MA		1.03	−0.06	VA	80.3	104.0	217.0
MMA–VA		3.02	2.62				
MA–VA		3.49	1.97				
Avg[b]		2.04	1.08				
Sty–MMA	Me stearate	0.261	0.95	Sty	0.0187	1.58	1.06
Sty–MA		0.328	0.67	MMA	0.0104	0.40	0.28
Sty–VA		1.16	−0.91	MA	0.157	0.70	0.75
MMA–MA		0.116	−1.07	VA	14.1	18.7	38.2
MMA–VA		0.523	2.70				
MA–VA		0.640	1.78				
Avg[b]		0.373	1.01				

[a] Sty signifies styrene; MMA, methyl methacrylate; MA, methyl acrylate; VA, vinyl acetate.

[b] Q_{tr} and e_{tr} for the styrene–vinyl acetate pairs were not included in the average.

Because n is almost unity (Fig. 3), rates of transfer in methyl oleate are roughly greater than those in methyl stearate by the factor $Q = 5.8$. The products QC_S for styrene in hexane and heptane at $100°C$[1a,14] are, respectively, 5.2 and 5.5×10^{-4}. Found values of C_S for 2-hexene and 2-heptene were[14] 3.6 and 3.2×10^{-4}, respectively, indicating qualitative correspondence.

When transfer data are available for a number of monomers toward a common solvent it is possible to calculate the transfer parameters, Q_{tr} and e_{tr}, corresponding to the copolymerization parameters of Price and Alfrey.[30] This was demonstrated some years ago by Fuhrman and Mesrobian[31] and has been applied to several solvents.[32-34] Values of Q_{tr} and e_{tr} are given in Table IV for all possible monomer pairs by using the relation

$$C_S = k_{tr}/k_{11} = Q_{tr}/Q_1 e^{-e_1(e_{tr}-e_1)} \tag{5}$$

Somewhat similar values of the polarity parameter e_{tr} were found for both solvents, especially if one compares the average values. The generally positive nature of e_{tr} suggests that both solvents act as strong electron acceptors in the transition state. Larger transfer constants should therefore be found for electron-donating styrene compared to electron withdrawing methyl methacrylate in these solvents, in spite of the opposite magnitudes of their propagation rate constants.[31] The ratios of the propagation constants and the absolute transfer constants (the latter given in Table IV) are lower for styrene and vinyl acetate in both solvents and thus are in harmony with this concept.[31] The calculated transfer constants in Table IV, computed using the average values given in the table by substitution in eq. (5), are in fairly good agreement with observed values.

It is possible to estimate k_t/k_p^2 by rearranging eq. (2)

$$k_t/k_p^2 = (1/\bar{X}_{n0} - C_M)/R_p/[M]^2 \tag{6}$$

Literature values for C_M for catalyzed experiments at $60°C$ were taken,[1b] and R_p was calculated by using a and K of Table III in eq. (3) at $[S]/[M] = 0$. Values of k_t/k_p^2 for comparison were obtained by using absolute values of k_t and k_p at $60°C$.[1c] Values of k_t/k_p^2 were, respectively, for methyl oleate, methyl stearate, literature: styrene $678, 619, 1\,163$; methyl methacrylate 38, 4.0, 36.2; methyl acrylate 861, 323, 2.2; vinyl acetate 144 (2.9 at $100°C$), 8.7, 2.8. Agreement was fair for all systems except methyl acrylate, considering the assumptions made and the experimental errors involved. Autoacceleration[35] may have affected the results for methyl acrylate.

Estimates of Monomer Transfer Constants for Monomers with Long Side Chains

Rough estimates may be obtained of the limiting degree of polymerization at zero rate for homologs of the four monomers containing 18 carbon side-chains. To accomplish this the alkane (or alkene) portion of the fatty acyl group of the solvent is considered to replace one hydrogen atom of the acyl methyl in vinyl acetate, the side-chain methyl in the acrylate and methacry-

late ester, and the p-hydrogen in styrene. The limiting degree of polymerization for the homologs becomes

$$\bar{X}_n \approx 1/C_{M(C_{18})} \approx 1/[C_M + (C_S - C_A)] \tag{7}$$

where C_M is the monomer transfer constant and C_A is the transfer constant of the radical toward ethyl acetate, in catalyzed experiments.[1a] This ester is taken as the approximate model for the contributions to transfer conferred by the labile groupings in the two solvents,[13] while C_S is the value of the transfer constant listed in Table III at solvent to monomer ratio of unity. Because C_A was not available for methyl acrylate, the value of the polymer transfer constant C_P,[a] equal to 0.5×10^{-4}, was taken as approximating the value, because the labile groups are similar. It is assumed in eq. (7) that all members of a homologous series have equal reactivity, an assumption that seems to be valid.[36,37] Values of $\bar{X}_n$ in eq. (7) were 8 400 and 2 700 for p-n-octadecyl- and p-oleylstyrene, respectively; 44 800 and 6 160 for n-octadecyl and oleyl methacrylate, respectively; 17 400 and 2 870 for n-octadecyl and oleyl acrylate, respectively; 254 and 46 for vinyl stearate and oleate, respectively. These constants are, of course, very approximate and cannot be confirmed directly. Degrees of polymerization for initiated low conversion poly(n-octadecyl acrylate) were about 650,[38] but values for inititated bulk polymers can be 1 000–1 500, and values for poly(vinyl stearate) prepared at this laboratory are usually about 150–200. Poly(vinyl oleate) is known to be oligomeric,[39] and poly-p-n-octadecyl-styrene apparently has a high molecular weight,[40] in qualitative agreement with predicted values. More significantly, these data suggest that the rate of polymerization primarily determines the molecular weight for monomers having long alkane or alkene side chains except for the vinyl esters. Here chain termination occurs primarily by transfer to monomer.[41]

SUMMARY AND CONCLUSIONS

Styrene, methyl methacrylate, methyl acrylate, and vinyl acetate were polymerized at 60°C in both methyl stearate and methyl oleate. Transfer constants were in the order, methyl methacrylate < styrene < methyl acrylate ≪ vinyl acetate, in both solvents. The presence of polar species in the transition state was supported by the order of reactivity. Transfer toward methyl oleate was about 5.8 times greater than that toward methyl stearate for all of the monomers. The internal allylic double bond of methyl oleate had about the same reactivity as the terminal unsaturation in N-allylstearamide. Rough estimates of the monomer transfer constants were derived for homopolymers having long alkane or alkene side chains. It was concluded that the rate of polymerization determined, for the most part, the degree of polymerization for the reactive monomers, but that the molecular weight of the vinyl esters was regulated primarily by transfer to monomer.

References

1. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Interscience, New York, 1966, (a) pp. II 79–II 126; (b) pp. II 79–II 82; (c) pp. II 57–II 82.

2. R. A. Gregg and F. R. Mayo, *J. Amer. Chem. Soc.*, **75**, 3530 (1953).

3. N. G. Saha, U. S. Nandi, and S. R. Palit, *J. Chem. Soc.*, **1956**, 427.

4. S. Basu, J. N. Sen and S. R. Palit, *Proc. Roy. Soc.* (London), **A202**, 485 (1950).

5. G. V. Schulz and L. Roberts-Nowakowska, *Makromol. Chem.*, **80**, 36 (1964).

6. S. R. Palit and S. K. Das, *Proc. Roy. Soc.* (London), **A226**, 82 (1954).

7. R. N. Chadha and G. S. Misra, *Trans. Faraday Soc.*, **54**, 1227 (1958).

8. J. T. Clarke, R. O. Howard, and W. H. Stockmayer, *Makromol. Chem.*, **44–46**, 427 (1961).

9. S. L. Kapur and R. M. Joshi, *J. Polym. Sci.*, **14**, 489 (1954).

10. N. Matsumoto, J. Ukida, G. Takayama, T. Eguchi, K. Mukumoto, K. Imai, Y. Kazusa, and M. Maeda, *Makromol. Chem.*, **32**, 13 (1959).

11. A. A. Vansheidt and G. Khardy, *Acta Chim. Acad. Sci. Hung.*, **20**, 381 (1959).

12. M. R. Gopalan and M. Santhappa, *J. Polym. Sci.*, **25**, 333 (1957).

13. A. J. Buselli, M. K. Lindemann, and C. E. Blades, *J. Polym. Sci.*, **28**, 485 (1958).

14. A. P. Titov and I. A. Livshits, *J. Gen. Chem. USSR*, **29**, 1605 (1959).

15. T. Otsu, A. Shimizu, and M. Imoto, *J. Polym. Sci. B*, **2**, 973 (1964).

16. E. F. Jordan, Jr., B. Artymyshyn, and A. N. Wrigley, *J. Polym. Sci. A-1*, **6**, 575 (1968).

17. E. F. Jordan, Jr., G. Riser, B. Artymyshyn, W. E. Parker, J. W. Pensabene, and A. N. Wrigley, *J. Appl. Polym. Sci.*, in preparation.

18. E. F. Jordan, Jr., G. R. Riser, W. E. Parker, and A. N. Wrigley, *J. Polym. Sci. A-2*, **4**, 975 (1966).

19. F. R. Mayo, *J. Amer. Chem. Soc.*, **65**, 2324 (1943).

20. S. R. Palit, S. R. Chattergee, and A. R. Mukhergee, in *Encyclopedia of Polymer Science and Technology*, Vol. 3, Interscience, New York, 1965, pp. 575–610.

21. P. W. Allen, F. M. Merritt, and J. Scanlan, *Trans. Faraday Soc.*, **51**, 95 (1954).

22. J. L. Kice, *J. Amer. Chem. Soc.*, **76**, 6274 (1954).

23. J. H. Baxendale, S. Bywater, and M. G. Evans, *J. Polym. Sci.*, **1**, 237 (1946).

24. S. W. Benson and A. M. North, *J. Amer. Chem. Soc.*, **81**, 1339 (1959).

25. A. M. North and G. A. Reed, *Trans. Faraday Soc.*, **57**, 859 (1961).

26. S. W. Benson and A. M. North, *J. Amer. Chem. Soc.*, **84**, 935 (1962).

27. F. De Schrijver and G. Smets, *J. Polym. Sci. A-1*, **4**, 2201 (1966).

28. G. C. Eastmond, in *Encyclopedia of Polymer Science and Technology*, Vol. 7, Interscience, New York, 1967, pp. 411–412.

29. J. E. Glass and N. L. Zutty, *J. Polym. Sci. A-1*, **4**, 1223 (1966).

30. T. Alfrey, Jr., and C. C. Price, *J. Polym. Sci*, **2**, 101 (1947).

31. N. H. Fuhrman and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **76**, 3281 (1954).

32. K. Katagiri, K. Uno, and S. Okamura, *J. Polym. Sci.*, **17**, 142 (1955).

33. M. Matsumoto and M. Maeda, *J. Polym. Sci.*, **17**, 438 (1955).

34. G. Platau, F. R. Eirich, R. B. Mesrobian, and A. E. Woodward, *J. Polym. Sci.*, **39**, 357 (1959).

35. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 126.

36. G. E. Ham, *Copolymerization*, Interscience, New York, 1964, p. 564.

37. E. F. Jordan, Jr., and A. N. Wrigley, *J. Appl. Polym. Sci.*, **8**, 527 (1964).

38. E. F. Jordan, Jr., H. A. Monroe, B. Artymyshyn, and A. N. Wrigley, *J. Amer. Oil Chemists Soc.*, **43**, 563 (1966).

39. S. A. Harrison and D. H. Wheeler, *J. Amer. Chem. Soc.*, **73**, 839 (1951).

40. C. G. Overberger, C. Frazier, J. Mandelman, and H. F. Smith, *J. Amer. Chem. Soc.*, **75**, 3326 (1953).

41. H. Kwart, H. S. Broadbent, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **72**, 1060 (1950).